

PATENT SPECIFICATION

766,677



Date of Application and Filing Complete

Specification: May 5, 1954.

No. 13094/54

Application made in United States of America on May 5, 1953.

Complete Specification Published: Jan. 23, 1957.

Index at Acceptance:—Class 2(3), C3A13A3(A1C; A1D; A2; A3; B1; B2; L), C3A13C(1B; 9; 10E).

International Classification:—C07b, c.

COMPLETE SPECIFICATION

Production of Alcohols.

We, MONSANTO CHEMICAL COMPANY, a Company organised under the Laws of the State of Delaware, United States of America, of 1700 South Second Street, City of St. Louis, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of alcohols containing at least four carbon atoms in the molecule. More particularly the invention relates to the provision of new catalysts or condensing agents for the Guerbet reaction.

The Guerbet reaction is well known to the organic chemist. According to this reaction a primary or secondary alcohol which contains a methylene group attached to the carbon atom of the carbinol group, i.e., the grouping $-\text{CH}_2\text{CHOH}-$ is condensed with itself to form as the principal product, an alcohol containing double the number of carbon atoms of the starting alcohol, for example, n-butanol is condensed to 2-ethylhexanol. Similarly, when two different alcohols of the same kind are condensed, the principal product is an alcohol containing the summation of the number of carbon atoms in the two reacting alcohols. Thus, a mixture of n-butanol and ethanol react to form 2-ethylhexanol (by condensation of two molecules of n-butanol), together with n-butanol (by condensation of two molecules of ethanol), n-hexanol and 2-ethylbutanol (by condensation of a molecule of n-butanol with a molecule of ethanol). A certain amount of condensation also occurs between the main higher alcohol produced and unreacted starting material, as well as between two molecules of the main higher alcohol product, and so on, forming a series of higher molecular weight alcohols by condensation which theoretically can involve any

two molecules present in the reaction mixture at a given time, so long as at least one of the molecules undergoing condensation contains a methylene group attached to the carbon atom of the carbinol group. It is only essential that one alcohol should contain the grouping $-\text{CH}_2\text{CHOH}-$ when two different alcohols are employed: the second alcohol may or may not contain such a grouping. As a practical matter, the quantity of alcohols higher than the main higher alcohol product is comparatively small.

The classical catalyst for the Guerbet reaction is sodium metal employed in the form of its alcoholate. It is known that the condensation occurs with liberation of hydrogen. However, the theories advanced for the particular mechanism of the Guerbet reaction, starting from the time of Guerbet's first work prior to 1900 up to the present day, are many and there is far from general agreement as to what reaction or reactions actually occur during the transformation of an alcohol of the type described to a higher alcohol. It seems apparent, however, that a plurality of reactions is involved, so that the process is particularly sensitive and not predictable as to the effect of a given catalytic material inasmuch as the postulated reactions are of varying types. For these reasons the reaction has been of great theoretical as well as practical interest to chemists who have investigated all phases thereof with numerous catalysts, reactants and reaction conditions. In addition to the alcohols formed by condensation of two molecules of alcohols present in the reaction mixture, side reactions result in the formation of other materials, principal of which are carboxylic acids (or salts thereof) and esters of carboxylic acids. It is ordinarily desirable to minimise formation of these by products.

An object of this invention is to provide new catalysts for the Guerbet reaction. An

other object is to effect the condensation of primary and secondary alcohols which contain a methylene group attached to the carbon atom of the carbinol group resulting in formation of higher alcohols. A further object is to increase the yield of the main higher alcohol formed by direct condensation of two mols of a starting alcohol of the type described and to minimise the concomitant formation of by-product acids and esters.

According to the present invention there is provided a process for the production of a primary or secondary alcohol having at least four carbon atoms in the molecule by condensing an alcohol containing the group $-CH_2CH(OH)-$ with itself, or with another alcohol which may or may not have such a group, by the Guerbet reaction in which there is used as condensation catalyst an alkali metal or alkaline earth metal phosphate which in 1% aqueous solution has a pH greater than 9.

More specifically the invention provides a process for the production of a primary or secondary alcohol having at least four carbon atoms in the molecule by condensation of one or two alcohols containing a $-CH_2CH(OH)-$ group and having from two to ten carbon atoms in the molecule which comprises heating said alcohol or alcohols in the presence of a dehydrating agent for alcohols and an alkali metal or alkaline earth metal phosphate which in 1% aqueous solution has a pH greater than 9.

According to this invention the Guerbet reaction is effected in the presence of added catalytic amounts of phosphates having in 1 per cent aqueous solution a pH greater than 9. The phosphates employed as catalysts are those of the alkali metals and the alkaline earth metals, preferably the former, provided the pH is as designated. Particularly preferred are the ortho and pyrophosphates. From the viewpoint of effectiveness and availability, the phosphates of potassium are preferred. Sodium phosphates meeting the stated requirements are also valuable. In general, the more electropositive the alkaline earth metal or the alkali metal, the more effective a given quantity of catalyst, e.g., a caesium phosphate is better than the corresponding sodium phosphate. However, the phosphates of potassium and sodium are usually the preferred catalysts for the present invention. Examples of phosphates that can be used as catalysts for the Guerbet reaction in the practice of the invention and which are preferred, are: tripotassium phosphate, dipotassium hydrogen phosphate, trisodium phosphate, tricalcium phosphate and tetrasodium and potassium pyrophosphates.

By the use of the above phosphates, we have obtained excellent results in carry-

ing out the Guerbet reaction with a variety of alcohols. The extent of conversion is high for this reaction, and the ultimate yields are very good. Formation of acid and ester by-products is very low.

Any catalytically effective amount of the chosen phosphate catalyst can be used, such as from 0.01 to 0.3 mol per mol of alcohol, but preferably the amount is from 0.05 to 0.25 mol of catalyst per mol of alcohol charged to the reaction. The optimum quantity of catalyst to be used will be dependent to some extent upon the particular catalyst chosen, the particular alcohol or mixture of alcohols to be condensed, and the temperature and time of reaction.

It is often desirable to employ additionally a dehydro-genation catalyst, preferably one of the known metal dehydro-genation catalysts, for example, copper, nickel, or copper chromite, or mixtures thereof. When a dehydrogenation catalyst is also employed, suitable amounts are from 1 to 5 per cent based on the weight of alcohol charged.

The optimum temperature to be used will vary with the alcohol charged, but is usually in the neighbourhood of the critical temperature of the particular alcohol. By way of example, the critical temperature of n-butanol is 287°C . and we have obtained excellent results in condensing n-butanol in accordance with this invention at $290-300^\circ\text{C}$. As a general rule, the reaction can be effected at a temperature of from 50°C . below the critical temperature of the alcohol to 50°C . above the critical temperature, the temperature used within this range, however, being chosen to give an economical rate of reaction without undue decomposition and side reactions. In some instances temperatures outside this range can be employed.

A suitable time of reaction for a batch process is from 4 to 10 hours, but in most instances 4 to 5 hours is sufficient and any considerable increase in time may actually lower the yield of the desired product. Ordinarily the reaction time required for a continuous flow-type of reaction system is considerably less than that required for a batch reaction. In a given instance a time of reaction will be chosen to provide a satisfactory economic balance between high conversion of starting alcohol to products other than the starting alcohol, and high ultimate yield of desired higher alcohol, i.e., a high proportion of the starting alcohol being converted to the desired higher alcohol product.

The process is commonly effected under pressure, but sometimes this is not necessary provided temperature and reaction times are properly selected to give significant extent of reaction at atmospheric pressure. For some alcohols the boiling temperature at

atmospheric pressure is not sufficiently high to give an adequate rate of reaction. However, the process is usually best effected under pressure and the autogenous pressure of the reaction mixture is quite suitable. If desired, the pressure can be increased above this value by the inclusion of added gas, such as an inert gas, i.e., nitrogen, or even an active gas, such as hydrogen.

It is preferred to effect the reaction under conditions enabling removal of water from the reaction system as water is formed during the reaction. Such removal of water is generally beneficial for high conversions and yields. One very effective method of obtaining such removal of water is by subjecting the reaction mixture to azeotropic distillation while the reaction proceeds, and separating out water from the condensate while returning the other components thereof to the reaction mixture. Such azeotropic distillation can be effected either in the presence or absence of a volatile entraining agent, for example, benzene or other inert hydrocarbon which aids the distillation of water from the reaction mixture. Whether or not to use such volatile entraining agent will depend upon the particular alcohol employed and the characteristics of the vapour-liquid equilibria for a given system. Alternatively, a chemical dehydrating agent for alcohols can be present in the reaction mixture to remove water as it is formed; a metal oxide stable under the reaction conditions, for example, calcium oxide or magnesium oxide, can be satisfactorily employed.

Since the Guerbet reaction is well known it is unnecessary to recite in detail the numerous alcohols which can be employed alone or in admixture with each other as the starting materials. The invention is broadly applicable to primary or secondary alcohols which contain a methylene group attached to the carbon atom which bears the hydroxyl group. The alcohol can be wholly aliphatic in character or can include an aromatic group. Alicyclic alcohols meeting the stated requirements are also applicable. Although the invention is usually applied to alcohols containing only carbon and hydrogen in addition to the oxygen of the hydroxyl groups, it can also be applied to alcohols coming within the general definition which also contain non-hydrocarbon groups which do not interfere with the desired condensation. The invention can be applied to an alcohol having an olefinic double bond although that bond may in some instances enter into reaction to some extent. The invention is applicable to primary and secondary alcohols having at least two carbon atoms, i.e., from ethanol upwards and subject only to reasonable thermal stability under the reaction conditions. Thus, a pri-

mary or secondary alcohol containing a methylene group attached to the carbinol group and having 20 carbon atoms in the molecule can be condensed with itself or with other alcohols within the general definition. Ordinarily, however, the invention is most desirably applied to alcohols containing from 2 to 10 carbon atoms in the molecule. Examples of alcohols which can be used include the following: ethanol, n-butanol, n-hexanol, n-octanol, propanol, i-propanol, octanol-2, 4-methyl-pentanol-2, beta-phenylethanol and cyclohexanol. Two of these can be reacted with each other, for example, n-butanol with ethanol. Further the following alcohols, although not themselves reactive, will react with a second alcohol which contains the $-\text{CH}_2\text{CHR}(\text{OH})$ grouping (in which R is a hydrogen atom or an alkyl or aryl group), to form higher alcohols: i-butanol, benzyl alcohol, 2-ethylhexanol-(1), 2-ethylbutanol-(1), cinnamyl alcohol, para-methoxybenzyl alcohol, for example, i-butanol with n-butanol.

The following examples illustrate the invention.

EXAMPLE 1

A mixture of 214.0 grams (2 mols) of n-hexanol and 53.0 grams (0.25 mol) of tri-potassium phosphate was refluxed at 158-160°C. under atmospheric pressure until 7.0 cc. of water formed and collected by separation from the reflux liquid being returned to the reaction flask. Then 8.0 grams of a nickel: copper dehydrogenation catalyst containing nickel and copper in a 44:56 ratio by weight was added to the reaction mixture, and the reaction continued for a period of 23 hours. Water formed during the reaction was separated out as rapidly as it was formed, 21.5 cc. being thus removed. The reaction mixture was then filtered and fractionated. 2-Butyloctanol in an amount of 88.8 grams was obtained, boiling point 106-108°C./3mm. of mercury, $d_4^{20}=0.891$. This is a conversion of 45.5 per cent of that theoretically possible if all of the n-hexanol charged were converted to 2-butyloctanol. (Conversions reported herein are all on this basis of per cent of theory). The amount of high boiling residue, which included alcohols higher than those containing 12 carbon atoms in the molecule, and esters, was 57.7 grams. The acid content was 3.1 grams. Unchanged n-hexanol recovered by distillation can be recharged to a continuous process or subjected to the same reaction in a separate batch.

EXAMPLE 2

Under conditions generally similar to those cited in Example 1, except that the total reflux time was only 10 hours, 214.0 grams of n-hexanol, 53.3 grams of tri-potassium phosphate, 8.0 grams of copper dehydrogenation catalyst, and 5.0 grams of

activated decolorising bone charcoal were refluxed at 157-168°C. and atmospheric pressure. The water which was removed as rapidly as formed in the reaction amounted 5 to 14.8 cc. The resultant liquid was filtered from the solids and then fractionated, yielding 56.6 grams of 2-butyloctanol and 20.0 grams of higher boiling material. The recovery of unchanged n-hexanol was 129.5 10 grams. The conversion to higher alcohol was 28.9 per cent of theory, with a yield of 66.8 per cent of theory.

EXAMPLE 3

A mixture of 444.0 grams of n-butanol 15 (6.0 mols), 53.5 grams of tripotassium phosphate and 20.0 grams of copper dehydrogenation catalyst was placed in a steel autoclave which was then sealed and heated to 290°C. for 5 hours with agitation by stirring. 20 At the end of this time, the autoclave was opened, the solids removed by filtration, and the organic material was distilled.

2-ethylhexanol was obtained in an amount of 94.0 grams, representing a conversion of 25 24.1 per cent of theory. Higher boiling material amounted to 20.0 grams.

EXAMPLE 4

An autoclave was charged with 444.0 grams (6.0 mols) of n-butanol, 53.0 grams 3 (0.25 mol) of tripotassium phosphate, 56.0 grams (1.0 mol) of calcium oxide and 20.0 grams of copper dehydrogenation catalyst. The reaction mixture was heated at 290°C. for 5 hours with agitation by stirring. The 35 mixture was then filtered and distilled, yielding 156.0 grams of 2-ethylhexanol (1.19 grams) and 22.5 grams of higher boiling material. Unreacted butanol amounting to 226.5 grams was recovered. The conversion of n-butanol to 2-ethylhexanol was 40 40.0 per cent of theory, with the yield amounting to 81.6 per cent of theory.

EXAMPLE 5

Under conditions similar to those cited 45 in Example 4, 444.0 grams of n-butanol (6.0 mols), 80.0 grams (0.37 mol) of tripotassium phosphate, 280 grams (0.5 mol) of calcium oxide, and 20.0 grams of copper dehydrogenation catalyst were heated to 290°C. for 5 50 5 hours. Upon cooling the mixture was filtered and the organic material was distilled. 2-ethylhexanol was obtained in the amount of 150.0 grams (1.15 mols), which is a conversion of 38.4 per cent of theory. 55 High boiling material amounted to 22.5 grams. Recovered unreacted butanol was 251.5 grams. When the phosphate was absent no condensation took place.

EXAMPLE 6

60 A stirred autoclave is charged with 6 mols of n-butanol 0.25 mol of tetrapotassium phosphate ($K_4P_2O_7$) and 0.5 mol of calcium oxide. The reaction mixture was maintained at 290°C. for 5 hours.

65 The resulting material was worked up as

described in the preceding Examples, resulting in a recovery of 50.0 grams of 2-ethylhexanol, which is a conversion of 12.8 per cent of theory. Higher boiling material amounted to 16.5 grams. 70

EXAMPLE 7

A stirred autoclave was charged with 6 mols of n-butanol, 0.25 mol of dipotassium orthophosphate and 0.5 mol of calcium oxide. The reaction mixture was maintained 75 at 290°C. for 5 hours.

As a result of the reaction there was obtained 92.0 grams (0.72 mol) of 2-ethylhexanol which is a conversion of 23.6 per cent of theory. Higher boiling materials 80 amounted to 18.5 grams.

EXAMPLE 8

A stirred reaction flask equipped with reflux condenser was charged with 303.0 grams (3.0 mols) of cyclohexanol, and 0.25 85 mol of tripotassium phosphate catalyst. The reaction mixture was refluxed for 10 hours at a reflux temperature ranging from 160 to 201°C. Water was separated out continuously from the condensed reflux, a total of 90 32.4 mol of water being thus removed.

On working up the reaction mixture, 154.5 grams of 2-cyclohexyl-1-cyclohexanol was recovered, *b.p.* 116-118°C. at 3 mm. of mercury. $n_D^{25} = 1.5037-8$; $d_4^{20} = 0.975$. 95 This represents a conversion of 56.5 per cent of theory. Also recovered was 40 grams of a solid by-product which was presumed to be impure dicyclohexyl-1-cyclohexanol.

What we claim is:—

1. A process for the production of a primary or secondary alcohol having at least four carbon atoms in the molecule by condensing an alcohol containing the group $-CH_2CH(OH)-$ with itself, or with another 105 alcohol which may or may not have such a group, by the Guerbet reaction in which there is used as condensation catalyst an alkali metal or alkaline earth metal phosphate which in 1% aqueous solution has a 110 pH greater than 9.

2. A process for the production of a primary or secondary alcohol having at least four carbon atoms in the molecule by the condensation of one or two alcohols containing a $-CH_2CH(OH)-$ group and having from 2 to 10 carbon atoms in the molecule which 115 comprises heating said alcohol or alcohols in the presence of a dehydrating agent for alcohols or a volatile entraining agent and an alkali or alkaline earth metal phosphate which in 1% aqueous solution has a pH 120 greater than 9.

3. A process according to either of Claims 1 or 2 in which the phosphate is 125 present in an amount from 0.05 to 0.25 mol per mol of alcohol present.

4. A process according to any of the preceding claims in which the phosphate is trisodium, tripotassium, or tricalcium phos- 130

phate, dipotassium hydrogen phosphate or tetrasodium or potassium pyrophosphate.

5. A process according to any of the preceding claims in which the alcohol is heated at from 50°C. below the critical temperature of the alcohol to 50°C. above the critical temperature under the autogeneously developed pressure.

6. A process according to any of the preceding claims in which there is additionally present a dehydrogenation catalyst.

7. A process according to Claim 6 in which the dehydrogenation catalyst com-

prises copper, nickel or copper chromite.

8. A process for the production of a primary or secondary alcohol having at least four carbon atoms in the molecule substantially as hereinbefore described with reference to any one of the Examples.

9. A primary or secondary alcohol when ever obtained by the process of any of the preceding claims.

STEVENS, LANGNER, PARRY &
ROLLINSON.

Chartered Patent Agents
and Agents for the Applicants.